

10/572677

IAP9 Rec'd PGT/PTO 20 MAR 2006

## Article 34 Amendment

AMENDMENT

(pursuant to Article 11 of the Japanese Patent Law)

To: Tomoko Hirono, Patent Office Examiner

1. International Application Classification: PCT/JP2004/013977

2. Applicant

Name: TEIJIN LIMITED

Address: 6-7, Minamihommachi 1-Chome, Chuo-ku, Osaka-shi, Osaka 541-0054 JAPAN

Nationality: JAPAN

Country of Residence: JAPAN

3. Representative

Name: Hideko MIHARA, Patent Attorney (9967)

c/o Teijin Intellectual Property Center Limited

1-1, Uchisaiwaicho 2-Chome, Chiyoda-ku

Tokyo 100-0011 JAPAN

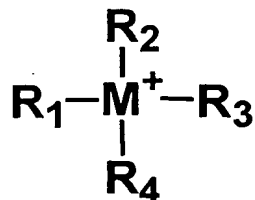
4. Object of the Amendment:

Specification and Claims

5. Content of the Amendment

Correction of the Specification and Claims as per the attached sheets. Specifically:

(1) The text "organic onium ion" on page 3, line 7 of the Specification is corrected to "organic onium ion represented by the following formula (1):



(1)

(wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently represent a C1-30 hydrocarbon group or a heteroatom-containing hydrocarbon group, M is a phosphorus atom to form a phosphonium ion, or M is a nitrogen atom and any of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> form a ring as a heteroaromatic ion, and at least a portion of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is an imide-substituted hydrocarbon group)".

(2) Lines 9-20 of page 3 of the Specification are deleted.

(3) Lines 3-11 of page 4 of the Specification are deleted.

(4) The text "For cases in which R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> form" on page 5, line 15 of the Specification is corrected to "For cases in which M is a nitrogen atom and any of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> form".

(5) The text "1,10-decanediol 1,4-cyclohexanedimethanol" on page 11, line 12 of the Specification is corrected to "1,10-decanediol, 1,4-cyclohexanedimethanol".

(6) The text "p-(hydroxyethoxybenzoic acid" on page 11, line 18 of the Specification is corrected to "p-hydroxyethoxybenzoic acid".

(7) The text "4,4'-diaminodiphenylsulfide, 4,4'-diaminodiphenylthioether" on page 12, line 20 of the Specification is corrected to "4,4'-diaminodiphenylthioether".

(8) The text "aliphatic aminocarboxylic acids such as 6-aminohexanoic acid and 12-aminododecanoic acid" on page 14, line 3 of the Specification is corrected to "aliphatic aminodicarboxylic acids such as 6-aminohexanedicarboxylic acid and 12-aminododecanedicarboxylic acid".

(9) The text "The present invention will now be explained in greater detail by the following examples, with the understanding that the invention is in no way restricted by these examples." on page 19, lines 14-15 of the Specification is deleted.

(10) The text "109 meqv" on page 19, line 17 of the Specification is corrected to "109 meq".

(11) The text "120 meqv" on page 19, line 19 of the Specification is corrected to "120 meq".

(12) The text "This was determined based on weight reduction rate calculated by the following formula, upon heating to 800°C in an air atmosphere at 20°C/min using a TG8120 differential thermogravimeter by Rigaku Corp." on page 19, lines 24-25 of the Specification is deleted.

(13) The text "10-bromodecamethylene phthalimide" on page 20, lines 18, 23 and 27 and page 21, line 7 of the Specification is corrected to "N-(10-bromodecyl) phthalimide".

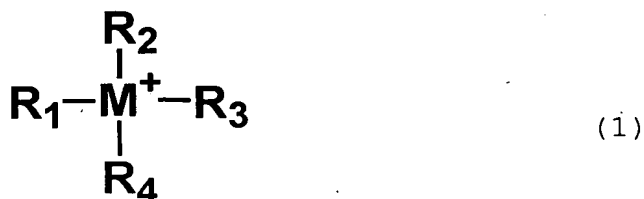
(14) The text "N-phthalimidedecamethylene-2-heptadecylimidazole bromide" on page 20, line 25 and page 21, line 1 of the Specification is corrected to "1-[10-(N-decylphthalimide)]-2-heptadecylimidazolium bromide".

(15) The text "N-phthalimidedecamethylene-trioctylphosphonium bromide" on page 21, lines 5 and 9 of the Specification is corrected to "10-(N-decylphthalimide)trioctylphosphonium bromide".

(16) The text "Example 1" on page 25, line 6 of the Specification is corrected to "Example 7".

(17) The text "chips" on page 25, line 6 of the Specification is corrected to "pellets".

(18) The text "organic onium ion" in claim 1 is corrected to "organic onium ion represented by the following formula (1):



(wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently represent a C1-30 hydrocarbon group or a heteroatom-containing hydrocarbon group, M is a phosphorus atom to form a phosphonium ion, or M is a nitrogen atom and any of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> form a ring as a heteroaromatic ion, and at least a portion of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is an imide-substituted hydrocarbon group)".

(19) Claim 2 is deleted.

(20) Claim 3 is deleted.

(21) The text "any one of claims 1 to 3" in claim 4 is corrected to "claim 1".

(22) The text "any one of claims 1 to 3" in claim 6 is corrected to "claim 1".

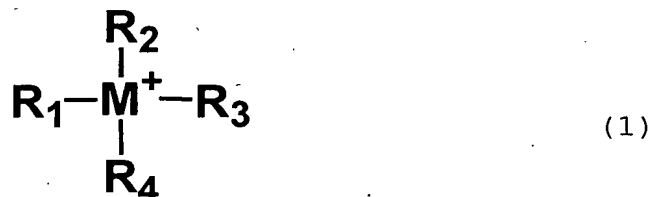
#### 6. List of Attached Documents

(1) Specification, pages 3, 4, 5, 11, 12, 14, 19, 20, 21 and 25

(2) Claims, pages 27 and 28

...Na-type fluorotaeniolite, Na-type fluorotetrasilicic mica and Li-type fluorotetrasilicic mica, as well as vermiculite, fluoro-vermiculite, halloysite and swelling mica. These may be natural or synthetic materials. Among these, smectite-based clay minerals such as montmorillonite and hectorite, Li-type fluorotaeniolite and Na-type fluorotetrasilicic mica are preferred for use from the standpoint of cationic exchange capacity.

The layered silicate is obtained by ion-exchange of a layered silicate with an organic onium ion represented by the following formula (1):



(wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently represent a C1-30 hydrocarbon group or a heteroatom-containing hydrocarbon group, M is a phosphorus atom to form a phosphonium ion, or M is a nitrogen atom and any of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> form a ring as a heteroaromatic ion, and at least a portion of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is an imide-substituted hydrocarbon group) at 50-100% of its ion-exchange capacity.

As C1-30 hydrocarbon groups there may be mentioned alkyl groups and aromatic groups. As alkyl groups there are preferred C1-18 alkyl groups, with preferred examples being methyl, ethyl, n-propyl, n-butyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl and n-octadecyl. As aromatic groups there are preferred phenyl, biphenyl, benzyl, tosyl and the like. These aromatic groups may also have substituents which do not affect their thermal stability, such as methyl, ethyl, fluorine or chlorine.

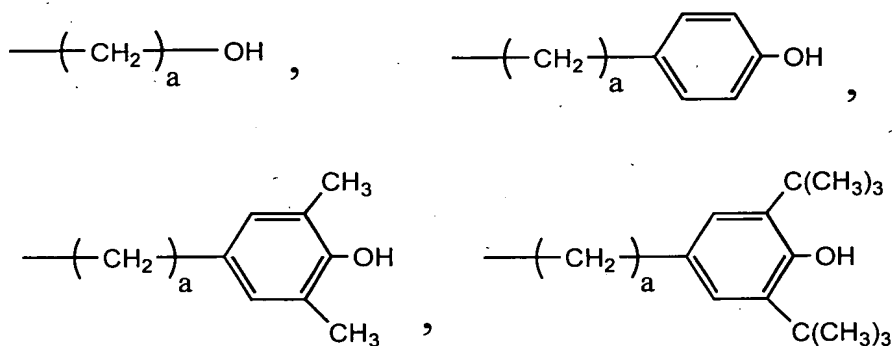
As specific examples of organic phosphonium ions wherein M is a phosphorus atom there may be mentioned

tetraethylphosphonium, triethylbenzylphosphonium, tetrabutylphosphonium, tetraoctylphosphonium, trimethyldecylphosphonium, trimethyldodecylphosphonium, trimethylhexadecylphosphonium, trimethyloctadecylphosphonium, tributylmethylphosphonium, tributyldodecylphosphonium, tributyloctadecylphosphonium, trioctylethylphosphonium, tributylhexadecylphosphonium, methyltriphenylphosphonium, ethyltriphenylphosphonium, diphenyldioctylphosphonium, triphenyloctadecylphosphonium, tetraphenylphosphonium and tributylallylphosphonium.

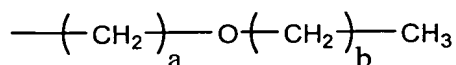
When formula (1) above represents hydrocarbon groups containing hetero atoms, at least some of the C1-30 hydrocarbon groups  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are preferably one or more selected from the group consisting of C1-30 hydroxyl-substituted hydrocarbon groups, alkoxy-substituted hydrocarbon groups, phenoxy-substituted hydrocarbon groups or imide-substituted hydrocarbon groups.

Hydrocarbon groups having hetero atom-containing substituents are listed below. (In these formulas,  $a$  and  $b$  are each independently integers of 1-29, and the numbers of carbon atoms in the formulas are no greater than 30).

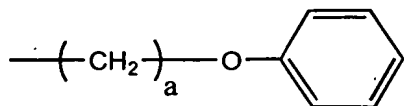
Hydroxyl-substituted hydrocarbon groups:



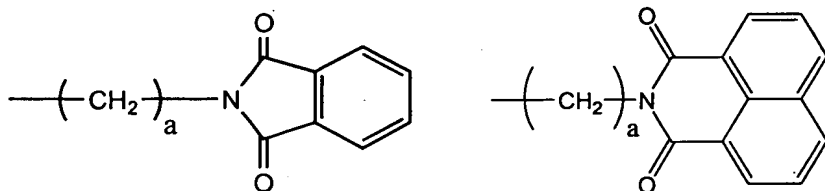
Alkoxy-substituted hydrocarbon group:



Phenoxy-substituted hydrocarbon group:



Imide-substituted hydrocarbon groups:



For cases in which M is a nitrogen atom and any of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  form a ring to constitute a heteroaromatic ion, there may be mentioned organic onium ions comprising pyridine derivatives such as pyridine, methylpyridine, ethylpyridine, dimethylpyridine, hydroxypyridine and dimethylaminopyridine, imidazole derivatives such as imidazole,...



4,4'-biphenyldicarboxylic acid, 2,2'-biphenyldicarboxylic acid, 4,4'-diphenyletherdicarboxylic acid, 4,4'-diphenylmethanedicarboxylic acid, 4,4'-diphenylsulfonedicarboxylic acid, 4,4'-diphenylisopropylidenedicarboxylic acid and 5-sodiumsulfoisophthalic acid, aliphatic dicarboxylic acids such as oxalic acid, succinic acid, adipic acid, sebacic acid, dodecanedicarboxylic acid, octadecanedicarboxylic acid, maleic acid and fumaric acid, and cyclic aliphatic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid. As diols there may be mentioned aliphatic diols such as ethylene glycol, 1,2-propyleneglycol, 1,3-propyleneglycol, 1,3-butanediol, 1,4-butanediol, 2,2-dimethylpropanediol, neopentyl glycol, 1,5-pentadiol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,4-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,2-cyclohexanedimethanol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, octamethylene glycol, diethylene glycol and dipropylene glycol, and diphenols such as hydroquinone, resorcinol, bisphenol A and 2,2-bis(2'-hydroxyethoxyphenyl)propane. As hydroxycarboxylic acids there may be mentioned aromatic hydroxycarboxylic acids such as p-hydroxybenzoic acid, p-hydroxyethoxybenzoic acid, 6-hydroxy-2-naphthoic acid, 7-hydroxy-2-naphthoic acid and 4'-hydroxybiphenyl-4-carboxylic acid.

As examples of preferred polyesters there may be mentioned polyethylene terephthalate (PET), polybutylene terephthalate, polycyclohexylenedimethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene naphthalate, polyethyleneisophthalate-terephthalate copolymer and p-hydroxybenzoic acid-6-hydroxy-2-naphthoic acid copolymer.

A polyamide is the product of polycondensation of a dicarboxylic acid and/or its derivative with a diamine, or an aminocarboxylic acid-derived product, or a copolymer of the

foregoing. As carboxylic acid components for polyamides there may be mentioned aliphatic dicarboxylic acids such as adipic acid, sebacic acid, dodecanedicarboxylic acid and octadecanedicarboxylic acid, cyclic aliphatic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid, and aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, orthophthalic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 4,4'-biphenyldicarboxylic acid, 2,2'-biphenyldicarboxylic acid, 4,4'-diphenyletherdicarboxylic acid, 4,4'-diphenylmethanedicarboxylic acid and 4,4'-diphenylsulfonedicarboxylic acid. As diamines there may be mentioned aliphatic diamines such as butanediamine, butanediamine, pentanediamine, hexanediamine, heptanediamine, nonanediamine and dodecanediamine, substituted aliphatic diamines such as trimethyl-1,6-hexanediamine, and aromatic diamines such as m-phenylenediamine, p-phenylenediamine, 1,4-diaminonaphthalene, 1,5-diaminonaphthalene, 1,8-diaminonaphthalene, 2,6-diaminonaphthalene, 2,7-diaminonaphthalene, 3,3'-diaminobiphenyl, 4,4'-diaminobiphenyl, 4,4'-diaminobenzophenone, 3,3'-diaminodiphenylether, 3,4'-diaminodiphenylether, 4,4'-diaminodiphenylether, 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfide, 4,4'-diaminodiphenylthioether, 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(3-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 1,1-bis(4-aminophenyl)ethane and 2,2-bis(4-aminophenyl)propane. These may be used alone or in combinations. As aminocarboxylic acids there may be mentioned aliphatic aminocarboxylic acids such as 6-aminohexanoic acid and 12-aminododecanoic acid, and aromatic aminocarboxylic acids such as p-aminobenzoic acid, 6-amino-2-naphthoic acid and 7-amino-2-naphthoic acid.

trimethyl-1,6-hexanediamine. These may be used alone or in combinations. As aminodicarboxylic acids there may be mentioned aliphatic aminodicarboxylic acids such as 6-aminohexanedicarboxylic acid and 12-aminododecanedicarboxylic acid.

Specific preferred examples of polyimides include paradodecamethylenepyromellitic imide and paraundecamethylenepyromellitic imide. Examples of preferred commercially available products include ULTEM (polyetherimide) and the like.

Examples of polycarbonates include polycarbonates composed of various bisphenols. As bisphenols there may be mentioned bis(4-hydroxyaryl)alkanes such as bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxyphenyl)heptane, 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, bis(4-hydroxyphenyl)phenylmethane, 4,4'-dihydroxyphenyl-1,1'-m-diisopropylbenzene and 4,4'-dihydroxyphenyl-9,9-fluorene, bis(hydroxyaryl)cycloalkanes such as 1,1-bis(4-hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1-methyl-1-(4-hydroxyphenyl)-4-(dimethyl-4-hydroxyphenyl)methyl-cyclohexane, 4-[1-[3-(4-hydroxyphenyl)-4-methylcyclohexyl]-1-methylethyl]-phenol, 4,4'-[1-methyl-4-(1-methylethyl)-1,3-cyclohexanediyl]bisphenol and 2,2,2',2'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spirobis-[1H-indene]-6,6'-diol, dihydroxyaryl ethers such as bis(4-hydroxyphenyl)ether, bis(4-hydroxy-3,5-dichlorophenyl)ether and 4,4'-dihydroxy-3,3'-dimethylphenyl ether,

The heat treatment temperature is preferably between the glass transition temperature and the melting point of the resin. A more preferred temperature range may be determined in consideration of the crystallization temperature of the obtained film and the physical properties of the obtained film.

#### Effect of the Invention

The ion-exchanged layered silicate of the invention can be satisfactorily dispersed in a thermoplastic resin composition. The thermoplastic resin composition of the invention has a high degree of dispersibility of the layered silicate and exhibits excellent heat resistance, gas barrier properties, flame retardance, elasticity and toughness, and can be used for various molded articles, fibers and films.

#### Examples

The present invention will now be explained in greater detail by the following examples, with the understanding that the invention is in no way restricted by these examples.

##### (1) Layered silicates:

Montmorillonite (Kunipia (sodium exchange volume: 109 meq/100 g), product of Kunimine Kogyo Co., Ltd.) was used. The interlaminar distance was 12.6 Å.

Fluoromica F (product of Co-Op Chemical Co., Ltd., sodium exchange volume: 120 meq/100 g) was used. The interlaminar distance was 9.8 Å.

(2) Cation-exchange rate: This was determined based on weight reduction rate calculated by the following formula, upon heating to 800°C in an air atmosphere at 20°C/min using a TG8120 differential thermogravimeter by Rigaku Corp.

$$\text{Cation-exchange rate (\%)} = \{W_f / (1 - W_f)\} / (M_{org} / M_{si}) \times 100 \quad (2)$$

(W<sub>f</sub> is the weight reduction rate according to differential thermogravimetric analysis of the layered silicate from 120°C

to 800°C at a temperature-elevating rate of 20°C/min,  $M_{org}$  is the molecular weight of the phosphonium ion, and  $M_{si}$  is the molecular weight per electrical charge of the cationic portion of the layered silicate. The molecular weight per electrical charge of the cationic portion of the layered silicate is the value calculated as the reciprocal of the cation-exchange capacity of the layered silicate (units: eq/g).)

(3) Weight ratio of thermoplastic resin and inorganic component of layered silicate in resin composition:

This was determined based on weight reduction rate calculated by the following formula, upon heating to 800°C in an air atmosphere at 20°C/min using a TG8120 differential thermogravimeter by Rigaku Corp.

(4) Thermal decomposition temperature: This was determined as the temperature to 5 wt% weight reduction, with heating to 800°C in nitrogen at 20°C/min using a TG8120 differential thermogravimeter by Rigaku Corp.

(5) Layered silicate interlaminar distance and average number of layers: This was calculated from the diffraction peak positions using a RAD-B powder X-ray diffracting device by Rigaku Corp. Calculation was performed using 0.9 as the Scherrer constant.

(6) Reduced viscosity ( $\eta_{sp}/C$ ): The reduced viscosity was measured using a phenol/tetrachloroethane (4:6 weight ratio) solution at a concentration of 1.2 g/dL and a temperature of 35°C.

(7) Specific surface area: The specific surface area was measured using  $N_2$  gas in a NOVA 1200 by Quantum Chrome Co., and divided by the weight of the sample.

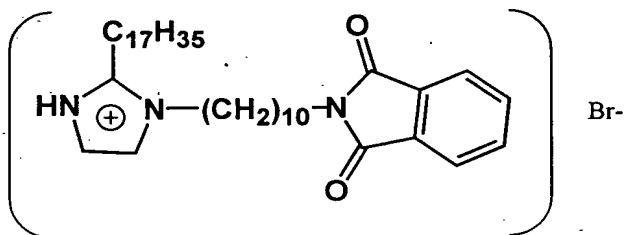
#### Reference Example 1: Synthesis of N-(10-bromodecyl)phthalimide

After placing 85 parts by weight of potassium phthalimide, 1008 parts by weight of 1,10-dibromodecane and 430 parts by weight of dimethylformamide (thoroughly dewatered) in a flask,

the mixture was stirred and heated at 100°C for 20 hours. After heating, all of the volatile components were removed and the residue was extracted with xylene. The volatile component was distilled off from the extracted solution, and the residue was allowed to stand at room temperature to obtain N-(10-bromodecyl) phthalimide crystals.

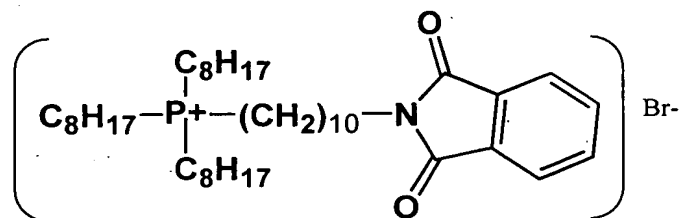
Reference Example 2: Synthesis of 1-[10-(N-decylphthalimide)]-2-heptadecylimidazolium bromide

After stirring together 20 parts by weight of 2-heptadecylimidazole and 24 parts by weight of the N-(10-bromodecyl) phthalimide obtained in Reference Example 1, stirring reaction was conducted for 8-10 hours at about 100°C to obtain 1-[10-(N-decylphthalimide)]-2-heptadecylimidazolium bromide (formula below).



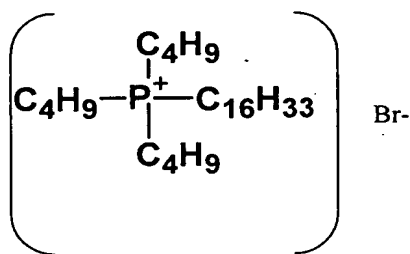
Reference Example 3: 10-(N-decylphthalimide)trioctylphosphonium bromide

After stirring together 20 parts by weight of trioctylphosphine and 20 parts by weight of the N-(10-bromodecyl) phthalimide obtained in Reference Example 1, stirring reaction was conducted for 8-10 hours at about 100°C to obtain 10-(N-decylphthalimide)trioctylphosphonium bromide (formula below).



Example 1: Synthesis of cation-exchanged layered silicate

After placing 100 parts by weight of Kunipia F and 3000 parts by weight of water in a flask, the mixture was heated and stirred at 80°C. To this mixture there was added a solution of 83 parts by weight of PX416 by Nihon Kagaku Co. (formula below):



dissolved in 300 parts by weight of water, and the mixture was additionally stirred for 3 hours at 80°C. The solid was filtered off from the mixture, washed three times with methanol and three times with water,

Table 3

		Example 7	Example 8	Example 9	Example 10
Resin		Poly(ethylene naphthalate)	Poly(ethylene naphthalate)	Poly(ethylene naphthalate)	Poly(ethylene naphthalate)
Reduced viscosity	$\eta_{sp}/C$	0.64	0.63	0.62	0.64
Layered silicate		Example 1	Example 2	Example 3	Example 4
Inorganic content	%	2	2	2	2
Melting point	$^{\circ}C$	267	268	270	270
Interlaminar distance	nm	2.7	2.7	2.5	2.3
Average no. of layers	-	4.3	4.4	4.7	4.5

Table 4

		Example 11	Example 12	Example 13
Resin		Poly(ethylene naphthalate)	Poly(ethylene naphthalate)	Polycarbonate
Reduced viscosity	$\eta_{sp}/C$	0.64	0.63	0.60
Layered silicate		Example 5	Example 6	Example 6
Inorganic content	%	2	2	2
Melting point	$^{\circ}C$	269	267	124
Interlaminar distance	nm	2.5	2.7	2.3
Average no. of layers	-	4.3	4.2	4.9

#### Examples 14,15: Fabrication of films

The strand-like pellets obtained in Example 7 were dried at 170 $^{\circ}C$  for 5 hours and supplied to an extruder hopper, melted at a melt temperature of 300 $^{\circ}C$  and passed through a 1.3 mm slit-shaped die for extrusion onto a rotating cooling drum with a surface temperature of 80 $^{\circ}C$ , to obtain an unstretched film. The unstretched film obtained in this manner was stretched to factors of MD x TD = 3.0 x 3.0 and 4.0 x 4.0 at a temperature of 150 $^{\circ}C$  to obtain a biaxially stretched film with a thickness of 15  $\mu m$ . The obtained biaxially stretched film was also heat-fixed for one minute at 205 $^{\circ}C$  to obtain a polyethylene naphthalate/layered silicate composite film. The



Young's moduli of the obtained films were, respectively, 7.1 GPa and 8.7 GPa in the MD directions.

#### Comparative Example 1

A layered silicate was obtained in the same manner as Example 1, except that the freeze drying was changed to vacuum drying at 150°C. The specific surface area was measured to be 1.70 m<sup>2</sup>/g.